National Renewable Energy Laboratory

Biomass Compositional Analysis

New Tools and Methods Supporting Biomass Utilization

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Biomass Analysis at NREL

Biomass Analysis Experts: more than 20 years of experience
Experienced in the analysis of a wide variety of biomass types
Standard Methods published through ASTM E48 Biotechnology
Standard Reference Materials available through NIST.

Importance of Biomass Analysis in Biomass Utilization

Natural heterogeneity of biomass

- Complex polymer matrix
- Inherent property of biomass
- Difficult to control in feedstock
  - Function of many variables
  - Feedstocks often residues of other process

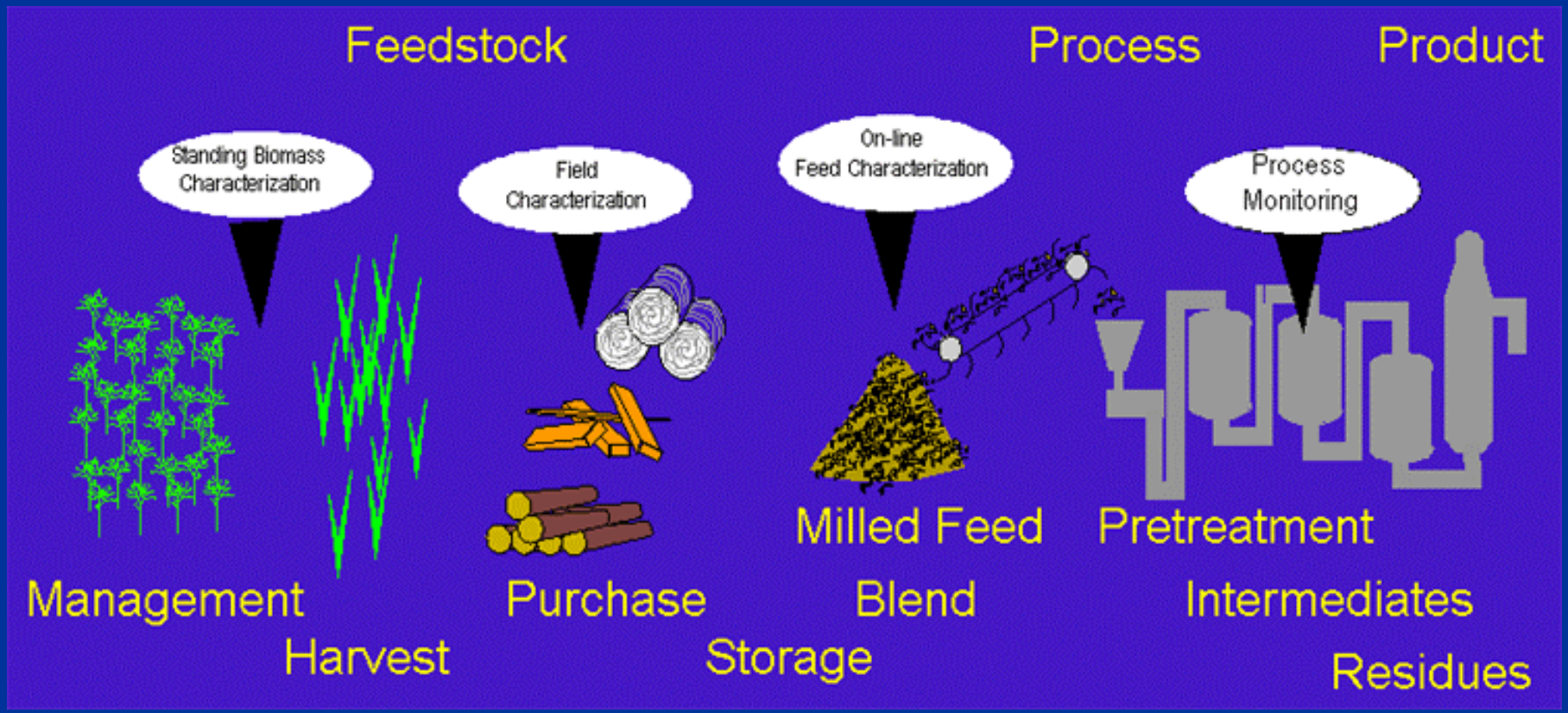
Significant challenge for emerging industries

- Complexity of biomass underestimated
- Traditional methods are expensive and slow
- New tools and methods needed

Advantages of Rapid Biomass Analysis

- Useful in industrial applications
  - Demonstrated technology
  - High impact / low risk
- Faster
  - Minutes instead of days
  - Minimal sample preparation
- Cheaper
  - $10 - $20 per sample
  - Compared to $800-$2,000 for wet analysis
- Better
  - Calibrated using best methods
  - Less operator dependent

Applications of Rapid Biomass Analysis



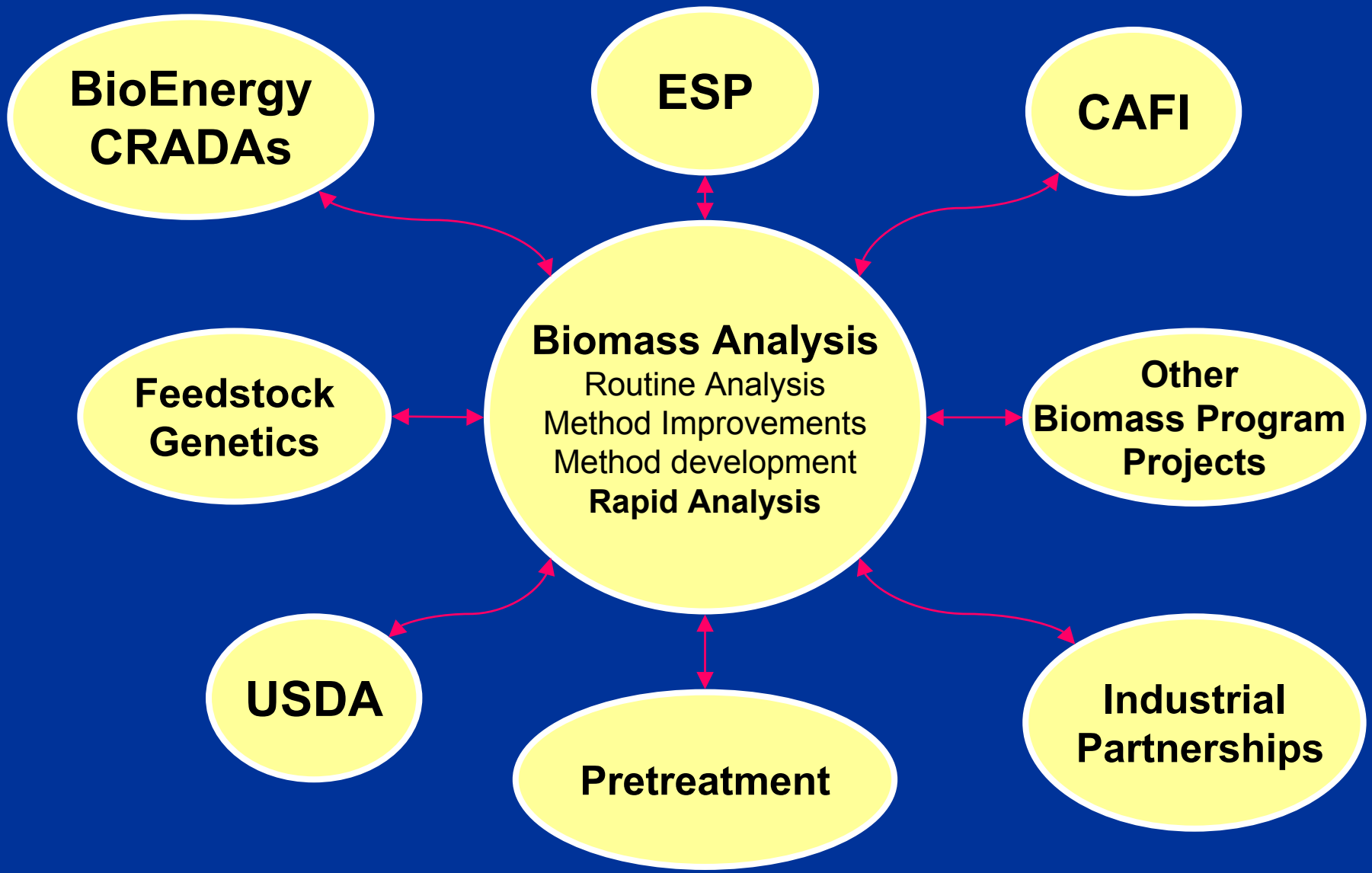
Real-time monitoring

Carbohydrates
Lignin
Protein
Moisture
Cell Mass

Ethanol
Other Products
Heating Value
Ethanol Production Capacity

Slide courtesy of B. Meglen

Integrated with Other Projects



Rapid Biomass Analysis Method Development Essentials

1. Calibration Samples
   - Determines the range of new method
   - Robust model requires approximately 100 samples
   - Should resemble samples to be analyzed
   - Account for variability (region, season, process, severity etc.)
   - Easier to obtain in research environments
   -
2. Chemical Characterization
   - Determines precision and accuracy of new method
   - Requires appropriate analytical methods
   - Most expensive part of method development

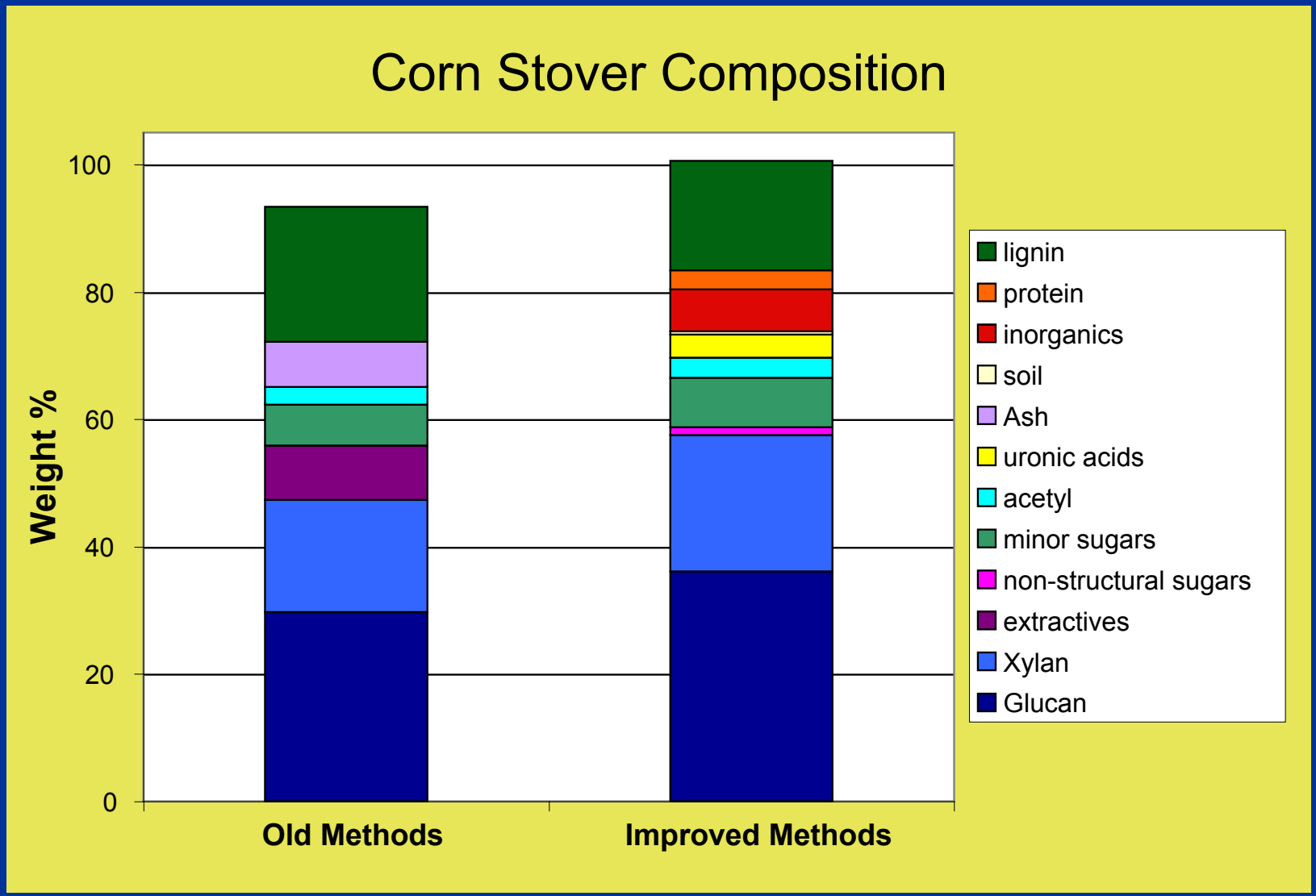
Rapid Biomass Analysis
Method Development Essentials

3. Rapid Technique
   - Determines speed and cost of new method
   - Should be robust and reproducible in collection environment
   - Must be sensitive to compositional changes

4. Multivariate Analysis
   - Translates spectroscopic data into compositional information

5. QA/QC
   - Guides use of new method
   - Calibration checks (include use of well characterized standard reference materials)
   - Sample screening (use of outlier flags, e.g. GH=3.0-----2.5 std dev-----99.5%population)

Improving Calibration Information



Wet Chemical Methods for Corn Stover Analysis

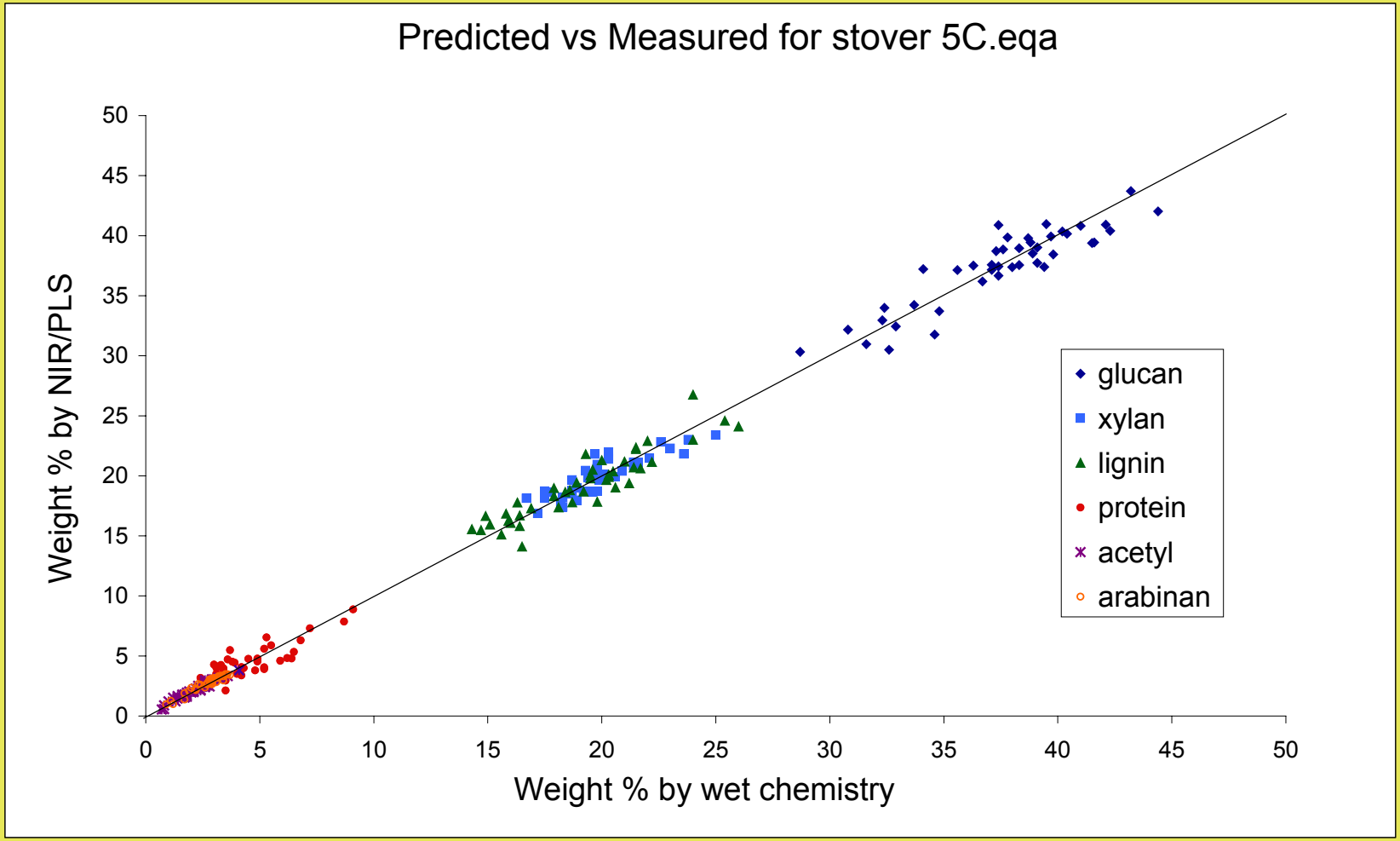
Methods in Use

- Carbohydrates
  - Glucan
  - Xylan
  - Arabinan
  - Mannan
  - Galactan
- Lignin
  - Acid Insoluble
  - Acid Soluble
- Protein (N%)
- Soil
- Structural Inorganics
- HMF / Furfural
- Acetyl groups

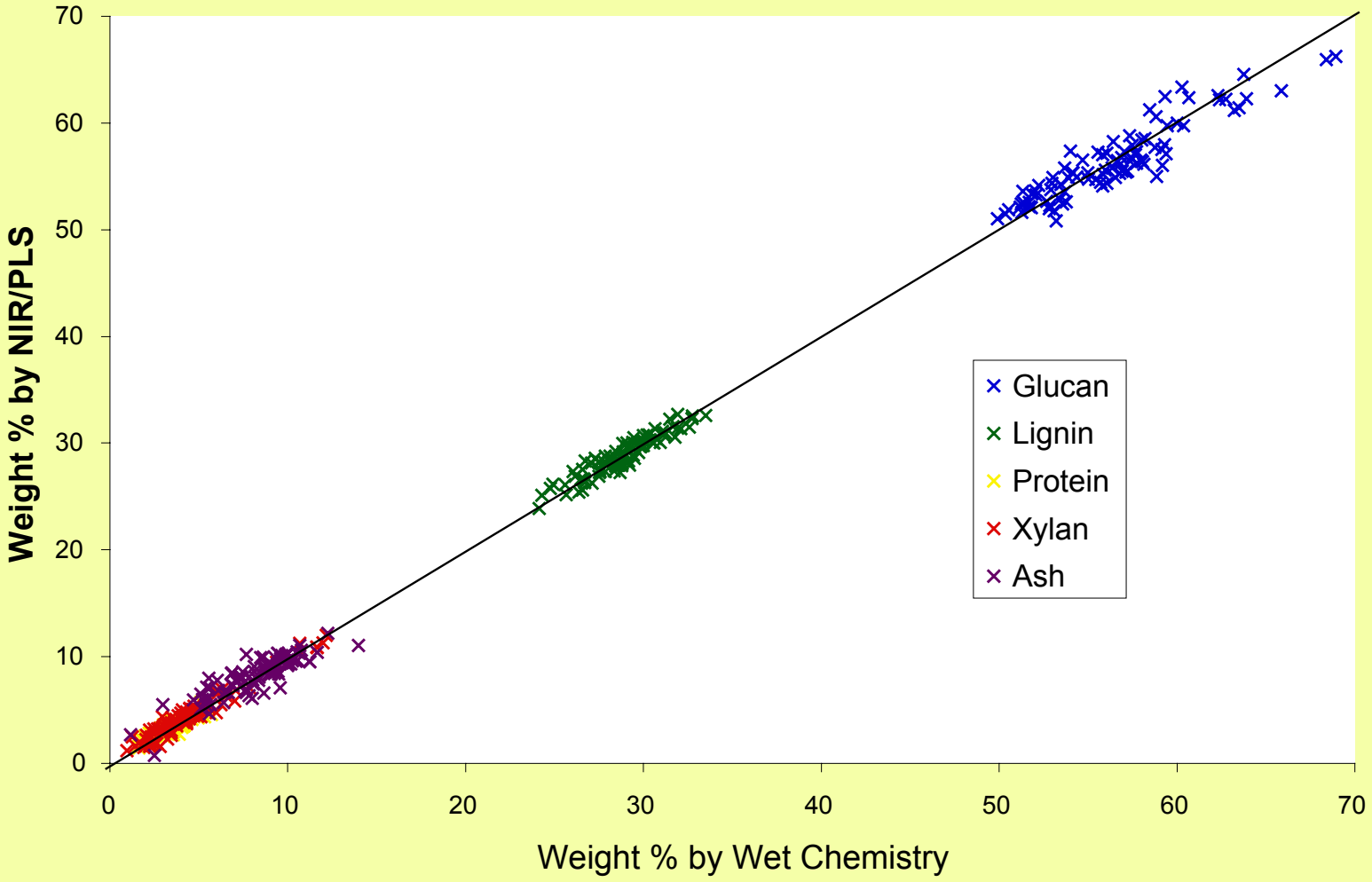
Methods being Developed or Improved

- Sucrose
- Uronic Acids / Pectins
- Amino Acids / Protein
- Nitrates / Nitrites
- Chlorophyll
- Protein Degradation Products
- Carbohydrate Degradation Products
- Physical properties

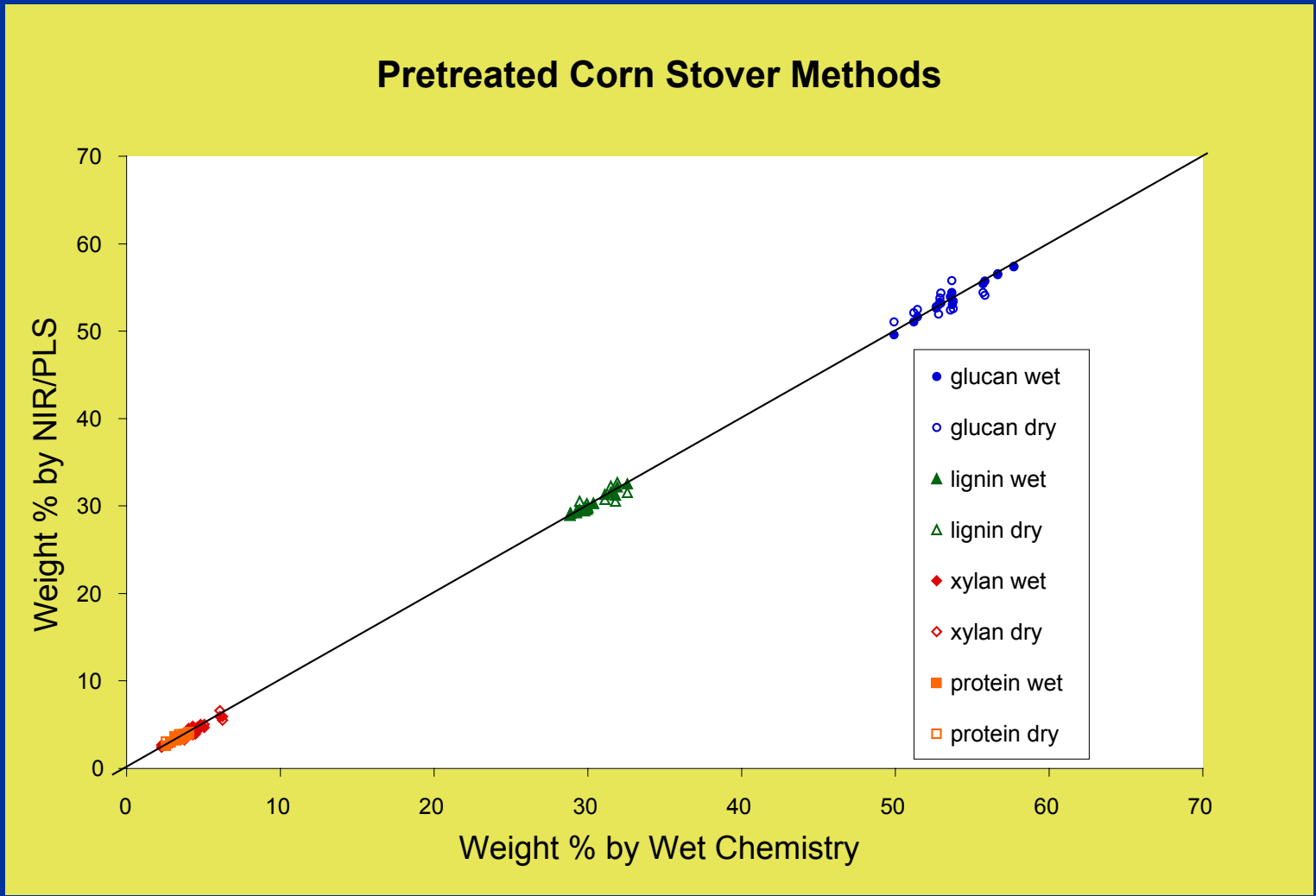
Corn Stover Feedstock NIR/PLS Method



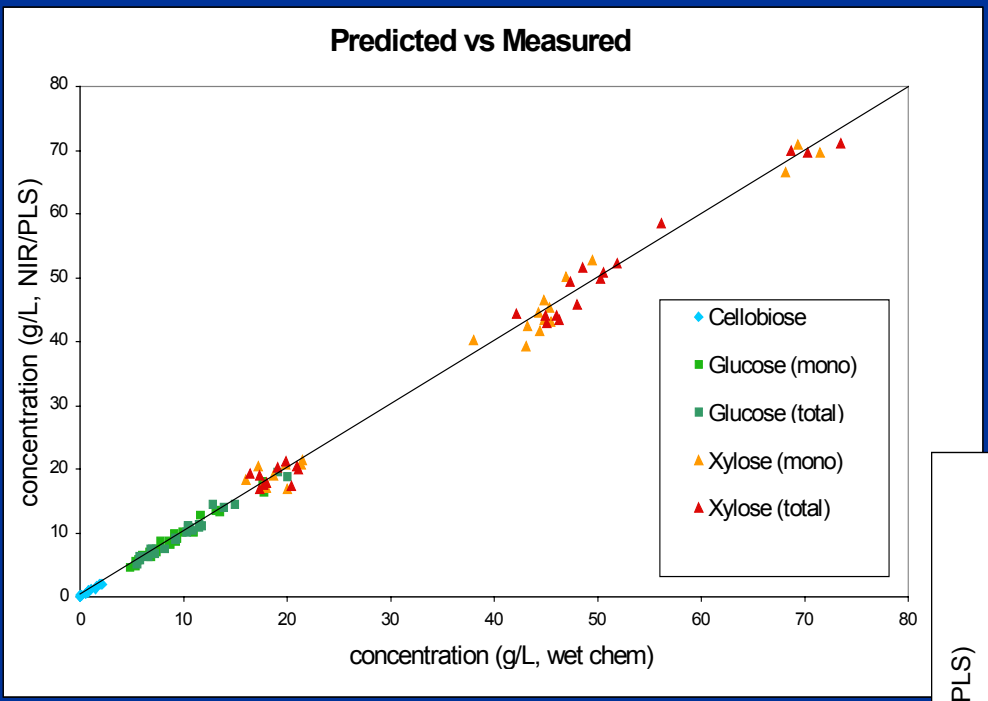
Pretreated Corn Stover : Dry solids



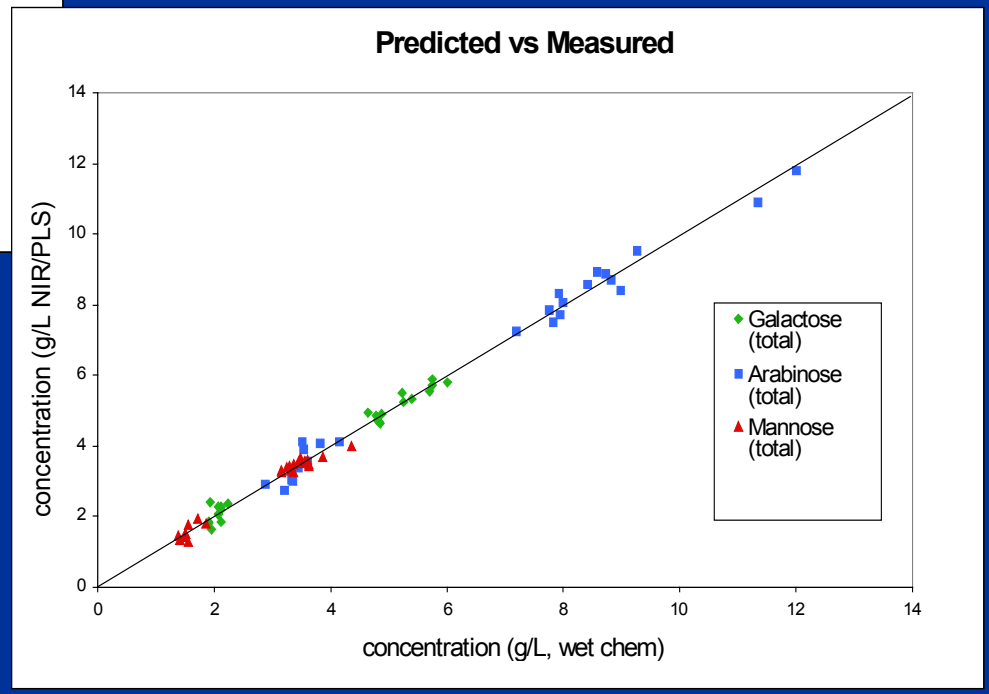
Pretreated Corn Stover: Slurry Method



Predicted vs. Measured Pretreatment: liquors1.eqa



- Sugars
  - Monomers and Oligomers
- Glycerol
- pH
- Acetic Acid
- HMF and Furfural

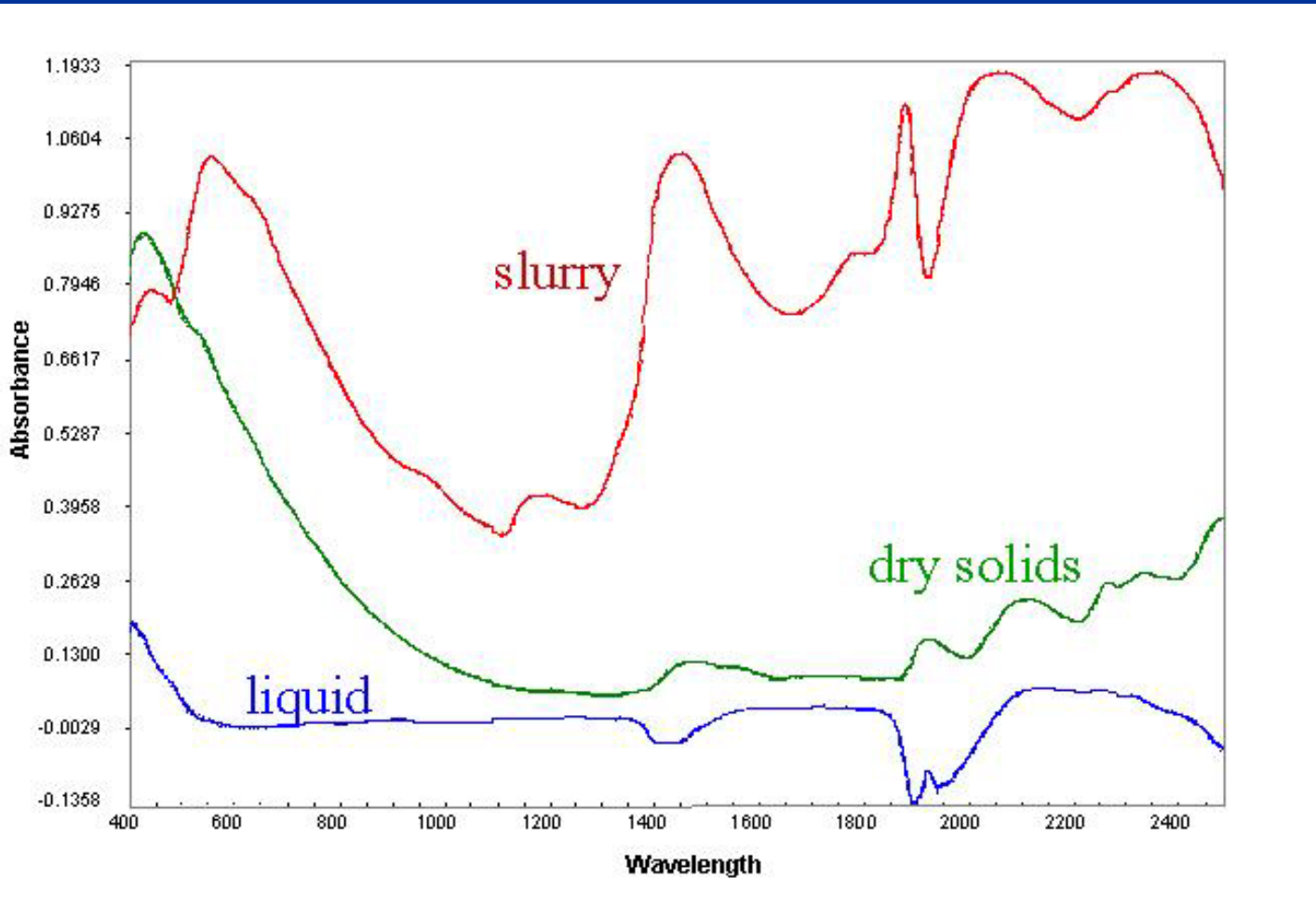


- Transmission spectroscopy
- Helma, flow-through quartz cuvette cell (pathlength of 0.5mm)
- Water used as reference
- Temperature Controlled at 60°C

Investigating Different Spectroscopic Techniques

Dry solid method

- Reflectance spectroscopy
- Slurry method
- Transflectance spectroscopy
- Liquid method
- Transmission spectroscopy



Improving Research
Providing New Levels of Information

- Rapid Analysis Methods allow experiments that require analysis of hundreds of samples
  - Not possible using traditional methods
    - Too expensive by wet chemical methods
      - $2,000/ sample x 1,000 samples = $2,000,000
    - NIR/PLS
      - $20/sample x 1,000 samples = $20,000
    - Too slow by wet chemical methods
      - Years to process 1,000 samples
    - NIR/PLS
      - 5-7 days to analyze 1,000 samples

Plans for Improving Wet Chemical Methods

- Expand slate of analyses
  - New constituents
  - New feedstocks
  - New processes
  - Physical properties measurements
- Improve current methods
  - Improve precision and accuracy
  - Improve total mass closures
  - Expand QA/QC methods
- Develop and validate feedstock-specific methods
  - Publish Validated methods through ASTM
  - Post on NREL website

Plans for Future Rapid Analysis Methods Development

- Demonstration in NREL Pilot Plant
  - On-line and at-line methods
  - Calibration transfer protocols
- Improve Field methods
  - Feedstock assessment
  - Genetic screening
- Expand slate of Rapid Analysis Methods
  - Different pretreatment chemistries
  - Corn Fiber, Corn Bran, DDG
  - SSF residues and fermentation samples
  - Field methods
  - Elemental Analysis and Higher Heating Value of process residues

Critical Issues

- High Cost
  - Cost of RA method development around $300,000
  - Methods are feedstock and process specific
  - Many methods needed to monitor entire biomass conversion process
- Resource issues
  - Current pace and scope of these projects cannot provide rapid analysis methods for industrial scale on-line applications in the near future

Biomass Rapid Analysis Network BRAN

- Consortium for Rapid Biomass Analysis Method Development
  - Fast-track rapid analysis method development
  - Expand calibrations for general applications
  - Share costs
    - Sample collection
    - Wet chemical analysis
    - Spectroscopic analysis
  - Consensus method validation
  - Creating and training future workforce
  - Communication network

Biomass Analysis Acknowledgements

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